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SOME POSSIBLE APPLICATIONS OF ISOTOPIC ANALYSES OF WATER TO HYDROLOGIC PROBLEMS

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The study of the water geochemical cycle by isotopic techniques began about thirty years ago, with determinations of the specific gravity of the water. This method was subject to great errors and the results were often unexplainable. However, it was possible to derive the idea that some systematic isotopic fractionations result from the processes related to the meteoric water cycle.

The importance of this idea is evident: isotopic fractionation makes it possible to recognize different steps in the water cycle, each step being traced by the deuterium and O^{18} contents of the corresponding water.

These studies greatly progressed only after 1946, with the construction of very sensitive mass-spectrometers, and it became possible to verify and develop some hypotheses proposed by authors such as Gilfillan, Brodsky, Neumann during the years from 1933 to 1940.

The studies of Kirshenbaum, Epstein, Dansgaard, Friedman, Craig etc. give the basis of the interpretation of isotopic variations in water samples which is now qualitatively satisfactory although quantitatively not yet very precise.

In a very simple and general model different isotopic compositions of precipitations are related with the temperature gradients in the air according to Rayleigh's distillation theory.

The average year-round isotopic composition of precipitation is related with the average temperature of formations of the rains: as a consequence latitude and altitude effects on isotopic composition of rains can be expected.

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A decreasing content of heavy isotopes is usually observed with increasing altitude or latitude. From the data recently reviewed by Dansgaard (1) variations of 0,6 - 0,9‰ in O^{18} content of rains per °C, are apparent: this corresponds to a variation of about 0,5‰ per 100 m (cf. 0,6‰ per 100 m found in North Greenland (2)).

The isotherm pattern greatly affects latitude gradients in different regions: so that a general value for this gradient is meaningless.

Seasonal isotopic variations in the precipitations over a region are also a consequence of the dependence of the isotopic composition upon the temperature, as Riesenfeld and Chang first observed. The summer precipitations are enriched in heavy isotopes with respect to the winter ones. This effect is larger in polar or continental regions (difference of about 10-15‰ in the O^{18} content) than in regions with oceanic or maritime climate (about 5-10‰).

The above summarized model can be used in spite of the fact that the isotopic composition of precipitation is also influenced by some factors which are difficult to evaluate such as contributions from evaporations of fresh waters, or precedent history of the vapour masses which condense to produce rains. Moreover the fractionation factor between the vapour and the condensed phases is uncertain in natural processes, chiefly owing to deviations from the equilibrium conditions. A liquid-vapour equilibrium seems to be established for atmospheric precipitation, while the process of free evaporation in nature is probably governed by kinetic factors (3).

The isotopic content in meteoric waters can be considered as a natural tracer allowing application to some geophysical problems particularly in regions with rather simple meteorologic situations.

This is the case in polar regions where isotopic methods have been applied to recognize the provenance of ice in icebergs (1) or the glaciers (4) and to detect a stratigraphy based on the iso-

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(1) Dansgaard, W., The Isotopic Composition of Natural Waters, Meddelelser om Grønland, 165, 1-120 (1961).

(2) Epstein, S., Sharp, R.P., Oxygen-Isotope Variations in the Malaspina and Saskatchewan Glaciers, Journ. Geol., 67, 88-102 (1959).

(3) Craig, H., Isotopic Variations in Meteoric Waters, Science, 133, 1702-1703 (1961).

(4) Gonfiantini, R., Togliatti, V., De Breuck, W., Picciotto, E., Tongiorgi, E., in preparation, (1962).

topic seasonal variations in the precipitations (5).

The application of isotopic techniques to hydrologic research sometimes becomes difficult owing to the complexity of the meteorological model and to water mixing in the soil. Possibly these difficulties explain the scarcity of works in this field of isotopic geochemistry. However, the isotopic method can sometimes be used successfully; here some applications to hydrological problems are reported and an extension of the results to more general problems is attempted.

Two or more waters in nature can be considered traced when they have different isotopic compositions. This may be the result of:

a) a difference in geographic origin connected with altitude or latitude effects;
b) a difference in the contribution of rains fallen in different periods during the year (seasonal effect);
c) a difference in evaporation which the waters may have undergone.

For some very simple hydrological problems it is sufficient to note a difference in the isotopic compositions of the bodies of water being studied, but usually the isotopic effects due to the above mentioned processes must be known. The isotopic fractionation cannot be exactly estimated on the basis of a model only giving a general picture of the phenomena; moreover a direct evaluation of the original isotopic composition of each water would require a long series of analyses. The problem must be then considered from a practical point of view in order to see how useful date easy to be measured can be obtained.

For this purpose let us consider the hydrologic budget in the general case of a region in which the water contribution given by the precipitations is equal to the sum of the losses due to the evaporation and to the run-off; the resident water is given by the aquifers and the lakes.

For the understanding of the isotopic balance of such a model, the following relation based on the isotopic mass conservation can be used (6):

$$\delta_s = \frac{Q_v \delta_v + Q_r \delta_r}{Q_v + Q_r} \qquad (1)$$

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(5) Epstein, S., Communication in "Symposium on the variations of the regime of existing glaciers", Obergurgl (Austria) (1962).

(6) The δ-notation is defined as the deviation in parts per mil of the ratios D/H or O^{18}/O^{16} in the sample with respect to the standard SMOW (standard mean pcean water). A δ = +3 (or -3) means that the sample is enriched (or depleted) in heavy isotopes of 3‰ relative to SMOW.

where δ_s is the mean composition of supply water, δ_v the mean composition of water lost by evaporation, δ_r the mean composition of water lost by run-off and Q_v and Q_r are the quantities of water removed by the evaporation and the run-off (7).

As fractionation can not occur because of the run-off mechanism a tracing of resident and run-off waters with respect to the supply water can be expected only by evaporation.

Three ways of evaporation have to be taken into account: (i) evaporation from water surfaces (lakes, rivers), (ii) transpiration of plants, (iii) evaporation from the soil.

During evaporation from water surfaces, light water evaporates preferentially with respect to heavy water so that the residual liquid is enriched in heavy isotopes becoming traced.

On the contrary as detectable isotopic fractionation can not be expected in the absorption of water by the plants, the water in the soil does not change its composition by mean of this process. The only isotopic effect due to transpiration is a tracing of water in the leaves.

In a similar way the evaporation from the soil removes water from the capillary fringe which absorbs continuously water from the under lying aquifer, probably without isotopic fractionation and any isotopic enrichment cannot be expected in the aqui fers.

A general constancy with time for the isotopic composition of aquifers has been observed in several wells in Tuscany and Latium. The absence of an appreciable enrichment during summer shows that, in spite of a large amount of water lost by evaporation from the soil and by transpiration from the plants, these processes are, as supposed, practically ineffective for isotopic tracing of ground water.

Let us now consider a watershed with a free evaporating water surface representing a small fraction of the total surface. In this case no significant fractionation can arise from all evaporation processes. Then it follows from (1) that the mean isotopic composition of the supplying waters (δ_s) must be the same as that of the run-off water (δ_r).

The average isotopic composition of a river water collected in the lowermost part of the watershed can therefore be representative of the mean isotopic composition of the supplying water in the watershed.

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(7) Gonfiantini, R., Togliatti, V., Tongiorgi E., in preparation (1962).

This happens when evaporation from the river itself is negligible: otherwise evaporation can trace river water with respect to supplying water.

This conclusion was confirmed by the study on oxygen composition of water samples collected during a year in three rivers of Tuscany: Arno, Serchio and Era. In this case summer evaporation is not important for the balance of these rivers because of their small volume-flow in this season: any summer enrichment disappears in weighing the yearly mean isotopic composition.

The average δ-values are in good agreement with the δ-values of the rains as they can be inferred considering the different characteristics of altitude and the geographical position of the three watersheds.

For the Serchio river, with a mountainous watershed, an average value for δ of -7.6 was found. For the Arno river in the watershed of which mountains, hills and plains are present, the δ was found to be -6.7. For the Era river, flowing in a hilly region, the δ was found to be -6.4.

Such differences in isotopic average composition due to latitude, altitude or continental effect on annual distribution of rains, can be considered as a primary tracing of waters.

A hydrological application arises from the possibility that different primarly traced waters inflowing into an area to be studied, can be distinguished one from another.

Within each zone any deviation from the value corresponding to the primarly traced water, can be considered as a second order tracing.

This one can depend on seasonal variations or local conditions of evaporation. For istance, differences in isotopic composition of river water samples collected at different times during the year correspond to a second order tracing as compared with the weighed mean annual isotopic composition of river water.

In the case of the above mentioned three rivers of Tuscany, different periods with characteristically traced waters can be considered with regard to the climatological condition of the region. The comparison between river isotopic composition and average flow during a ten days period before each sampling (figures I and II: curves 1 and 2) shows how the seasonal variation in isotopic composition of rivers can be related to the isotopic composition of the rain.

Winter and spring rains falling on a saturated basin cause a sudden strong increase in the volume flow. The light water observed in these periods obviously reflects the precipitation

on the watershed during preceding days. In this way no general definite value can be considered for winter and spring waters in a river as they are strictly related with rainfalls. But during relatively dry periods in winter and in spring the isotopic composition of the river water tends to assume a constant value.

Later in time in connection with the summer dry period, the δ -values increase and rapidly approach the maximum observed in September. The summer isotopic composition of the river water cannot be ascribed to high content in heavy isotopes in summer rains as they have been observed also during summers without any precipitation.

Finally autumn rain causes both an increase in volume-flow and a decrease in δ -values. These are nearly constant and similar to the values observed during the dry periods of winter and spring.

Concluding, the three considered rivers show two characteristic δ -values: the summer and the autumn ones. The first one is higher than the autumn value, which in turn is nearly the same as that observed as a constant value in aquifers.

This last fact can be understood taking into account that: (i) The summer lowering of the level of aquifers is compensated by autumn rains (from curves 2 and 3 in figures I and II it can be seen that the volume-flow of the rivers in September is not increased in spite of the large amount of precipitations in this month). Furthermore the largest part of the precipitations reaches aquifers in the season of dormant vegetation. (ii) Winter and spring rainfalls flow in greatest part on a saturated soil and summer rains, if present, are negligible; so the main contribution must be due to the autumn precipitations. Possible contributions in other seasons does not affect the isotopic composition of the water since mixing in the aquifers occurs.

As a consequence of the filling mechanism of aquifers the average isotopic composition of their water cannot be the same as the year weighed average composition of water in rivers.

In Tuscany however these two values are very close. This is because autumn and spring precipitations which have similar isotopic composition represent the greatest part of the total amount during the year. Furthermore a great amount of water flows slowly underground reaching surface watercourses after a long time. This contribution can be responsible of the fact that in dry periods during winter and spring the water of rivers in Tuscany tends to have the same isotopic composition of the autumn water.

From these facts it results that, instead of checking the isotopic composition of water in a river over a year, it would be possible to obtain information on the first order tracing in rivers of Tuscany only from a few samples collected in the aquifers and in the rivers during the autumn. In any case a proper period for sampling can be deduced from the annual distribution of precipitations.

The summer value of the isotopic composition of water in the rivers of Tuscany must be considered in relation to the absence of precipitations in this season. In this condition one can write (7):

$$\delta_r = \delta_a + \frac{Q_v}{Q_a}(\alpha - 1)1000 \qquad (2)$$

where Q_v is the quantity of water evaporated from the river, Q_a is the quantity supplied to the river by aquifers, δ_r is the isotopic composition of water in the river, δ_a is the isotopic composition of water in the aquifers and α (about 1.01 for oxygen) is the fractionation factor between liquid and vapour water.

When evaporation from the rivers is far from negligible, as in summer, it is evident from (2) that δ_r must be more positive than δ_a, as found in the rivers of Tuscany.

The evaluation of the amount of water drained by the river on the basis of (2) can be affected by great errors due to the uncertainty on δ-value; but relative evaluation of drained water along the river avoids this difficulty.

As a particular case it appears that when the summer isotopic composition along a river is constant, as has been observed for the level part of the course of the Arno river, the drainage from aquifers must be constant too.

To obtain these conclusions it is necessary to assume that, after the last spring rains, there has been time enough for river waters to acquire the composition that they would have in steady conditions. This assumption is confirmed not only by theoretical considerations but also from evidence that, in all the observed cases, the seasonal curve achieves the summer maximum in an asymptotic way.

In the case of large water surfaces hydrological applications of tracing due to evaporation become more evident.

A model of the isotopic enrichment has been developed (8). The isotopic composition δ_l of a lake with a constant level and in steady conditions depends on the isotopic composition δ_s of the supplying water, on the fractionation factor α between liquid and vapour and on the ratio X between the amount of water lost by evaporation and the amount of supplying water:

$$\delta_l = \delta_s + X(\alpha - 1)1000 \qquad (3)$$

If the evaporation is very low with respect to the water supply, and the level is kept constant by an important outlet, the X-value is practically zero and the isotopic composition of the lake is equal to δ_s; on the contrary if there is not any outlet and water is lost only by evaporation, the X-value is equal to 1 and the maximum enrichment in heavy isotopes is reached by the

(8) Gonfiantini R., Togliatti V., Tongiorgi E., Il rapporto O^{18}/O^{16} nell'acqua del Lago di Bracciano, Notiziario CNEN, Giugno 1962.

lake. As a consequence the water in the lake can have an isotopic oxygen composition varying from that of supplying water to another one about 10 δ-unities more positive.

Some lakes of Central Italy, practically without outlet, have water with a high oxygen-18 content, as example δ = +2.0 in Trasimeno lake, δ = +0.7 in Bracciano lake. In the same region aquifers and rivers have an isotopic composition suggesting a value of δ = -6.5 for the average isotopic composition of supplying water.

This remarkable tracing have been succefully used in order to establish if and in which amount the water of the lake contributes to the aquifers surrounding the lake.

It must be noted that in so far as the maximum depth of Bracciano lake is 160 m, the isotopic composition of the water is constant. On the contrary, surface samples show small seasonal variations from the value observed in depth.

From these data can be deduced that the lake has attained an isotopic steady state.

On the basis of the amplitude of the seasonal variations in surface waters, a mixing rate of about 10 meters per year has been extimated.

Any sudden change in the hydric budget of a lake will be reflected in a tracing of the upper layers with respect to the underlying layers. In the isotopic composition of water at increasing depth a record of the history of the lake is so preserved for a period of time depending on depth and mixing rate.

The examples and considerations as given show that in some cases with the isotopic methods results that are difficult or impossible by other methods, can be obtained.

The few data available at present with regard to the variations in the isotopic composition of natural waters reduce the number of possible hydrological applications. In addition, because of the not yet perfect knowledge of the tracing processes' mechanism, with particular regard to the values of the fractionation factors between liquid and vapour in natural conditions, the possibilities of surveying are further limited.

In these conditions no general rule for isotopic research in hydrology can be established; in every case the methods of solving the particular problems will be suggested either by the local interests on informations which can be obtained or by the possibility of knowledge of the necessary parameters.

A research which in some conditions cannot assure results, can be fruitful if undertaken in regions in which geographical or climatic conditions cause a strong tracing of water.

The results obtained in a region not favourable from this point of view confirm the conviction on the utility of isotopic methods.

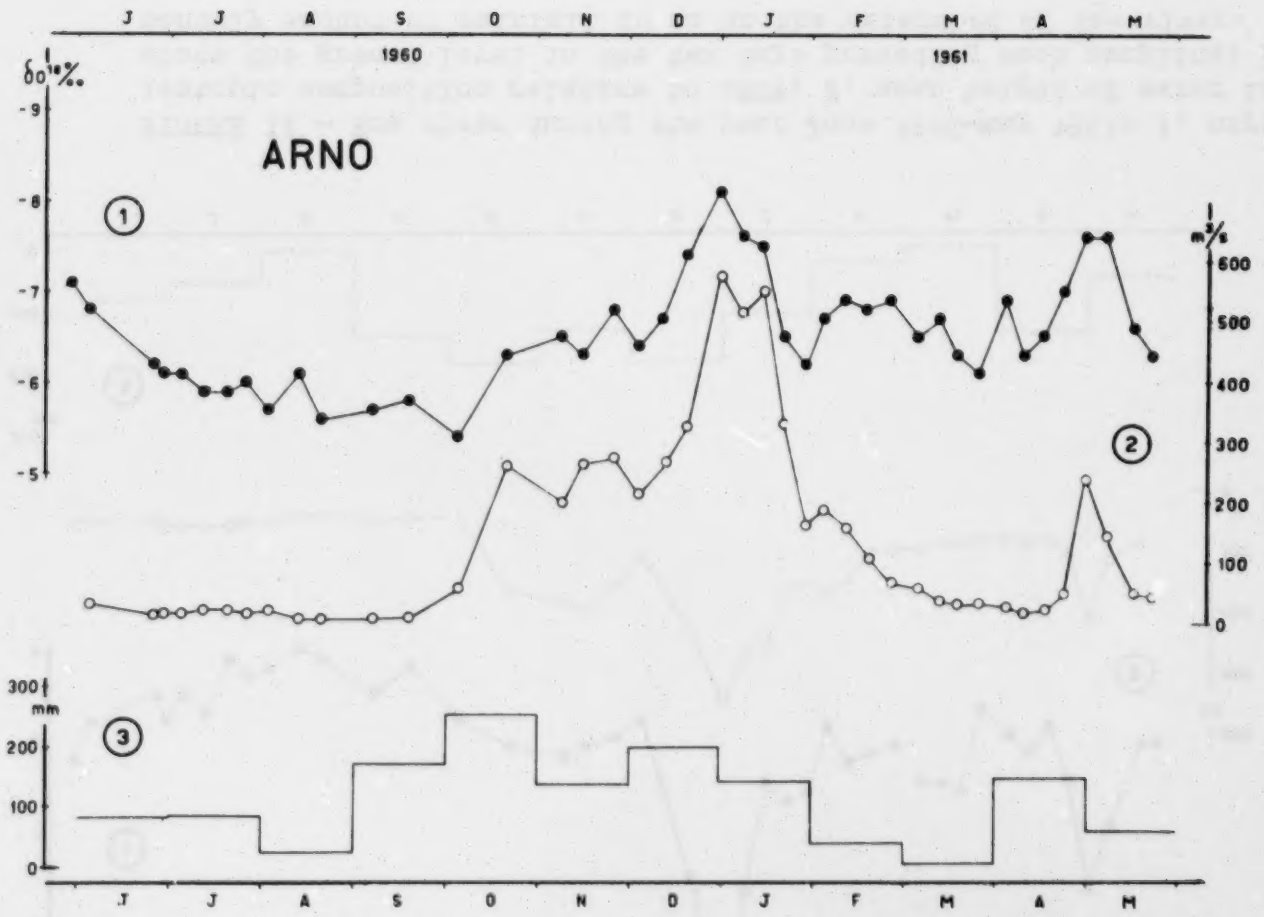

FIGURE I - Arno river during the year June 1960-May 1961: 1, oxygen isotopic composition relative to SMOW; 2, mean volume-flow in m /sec in the ten days preceding each sampling; 3, montly amount of rainfall in mm on the watershed of the river.

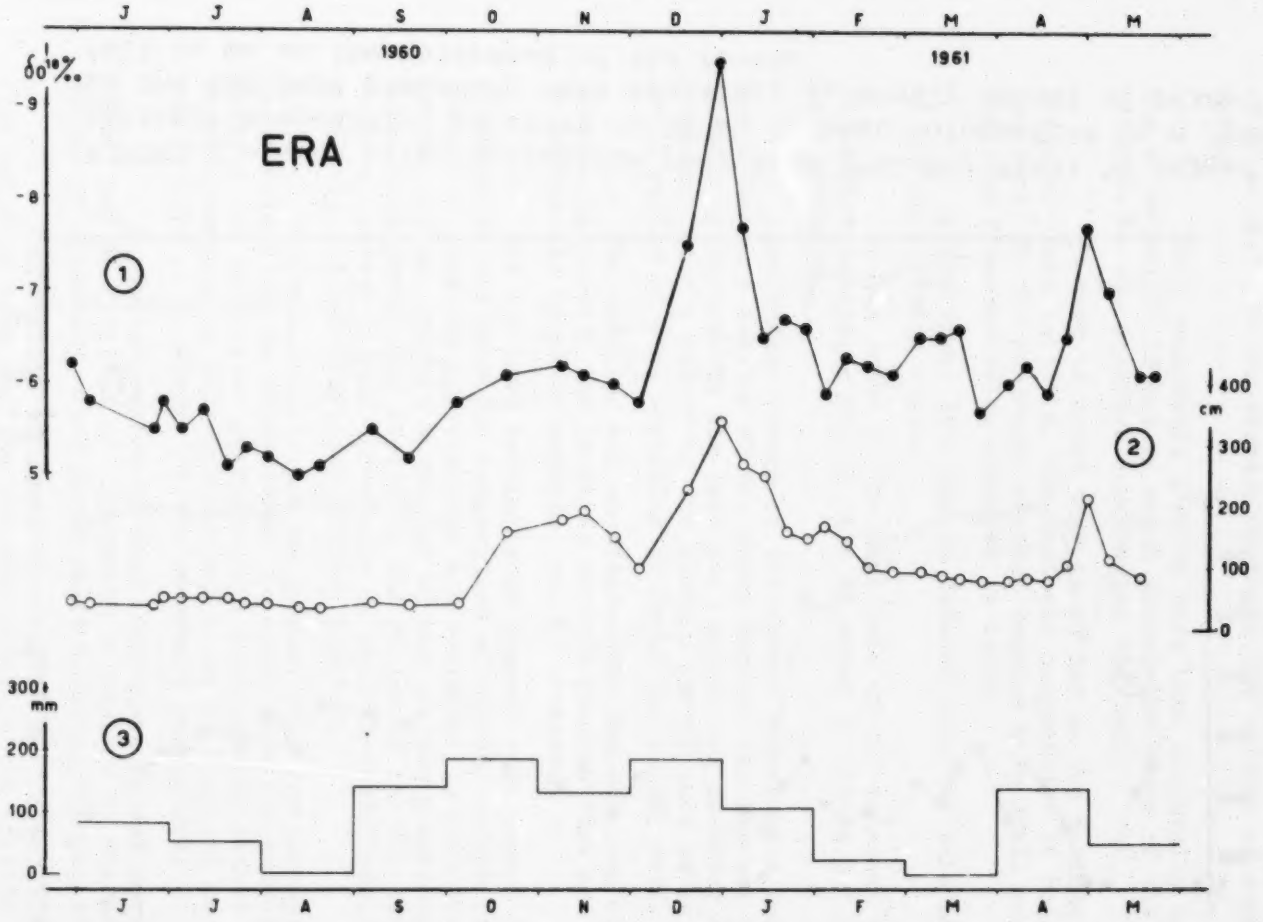

FIGURE II - Era river during the year June 1960-May 1961: 1, oxygen isotopic composition relative to SMOW; 2, mean height of water in cm above the ground level in the ten days preceding each sampling; 3, monthly amount of rainfall in mm on the watershed of the river.

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